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SOME ASPECTS OF NEW POLYMERS FOR DIELECTRICS

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The Air Force requirements for new materials, and new electric or dielectric materials, are imposed to a great extent by the higher speeds of current and future weapon systems. This, together with the need to miniaturize equipment, means in most cases higher ambient temperatures for dielectric materials.

A wide variety of dielectric materials are already available covering not only the most diversified applications such as radomes, wire and cable insulation, capacitor dielectrics, potting materials, interlayers, etc. but also wide temperature ranges, from room temperature to far above 400°F for continuous operation over at least several years. This means even considerably higher temperatures for short-time applications. While most of the conventional organic polymers are applicable to temperatures up to about 300°F for continuous use, the silicone resins and rubbers are presently the only materials to be flexible and resilient and to have thermal stabilities of 400 to 480°F for longer periods of time. Still higher temperatures for longer periods of time are only tolerated by materials like glass, quartz, mica, ceramics, and certain oxides. These materials, however, are not flexible and are difficult to form, modify, and machine. It would be of considerable value to find new materials, which approach the thermal stability of ceramics and related materials and at the same time have the mechanical properties of plastics or elastomers.

The electrical characteristics required are very different depending upon the application, and in certain cases the electrical properties of a dielectric material are even more or less unimportant. This is the case with certain applications of embedding resins, which possibly have to have flexibility, strength, moisture impermeability, but not necessarily superior dielectric properties. However, generally one or more of the following properties are required: stable dielectric constant (either high or low) over a temperature and/or frequency range of interest, low dielectric loss over temperature and/or frequency range of interest, high volume resistivity, and high dielectric strength.

Do we know how to accomplish these properties when synthesizing a new polymer? So far not too much knowledge has been accumulated to predict the dielectric properties of unknown chemical structures, (figure 1). One of the few things we are able to do is to predict the order of magnitude of the dielectric constant from the dipole concentration, which requires known data from related structures to first estimate the dipole moment of the unknown material. The dipole moment of a material depends upon the types of chemical groups or elements present in the molecule. The bond between each two elements in the molecule can be considered as an electrical dipole, and the product of the total positive or negative charge at the center of gravity by the distance between the centers of gravity is the dipole moment. Chemical groups with high and low dipole moments are known and can be introduced into a polymer to change its dielectric constant. Furthermore, the dielectric dispersion and the loss factor maximum is related to the second order transition point. The second order transition point is the temperature, at which, upon cooling, the substance converts to the glassy state and the microbrownian movement of chain segments ends, considering an observation or relaxation time of the order of 10^3 seconds. It is therefore a measure of rigidity in the structure, and the

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second order transition temperature rises with the introduction of sterically rigid elements or with groups, which introduce strong secondary bonding forces. It can be seen from figure 1 that the dielectric relaxation temperatures measured at different frequencies can be extrapolated to the second order transition point at a frequency or relaxation time of 10^3 seconds. There is only a limited possibility, however, that the temperature of dielectric relaxation from the second order transition point can be predicted because the slopes of the curves are different. The second order transition point itself of a projected new structure can only be predicted when several polymers of a series are already known. At the second order transition point the rate of increase or decrease of a number of physical properties, and also of the resistivity, changes abruptly. This correlates the resistivity to the second order transition point, as can be seen under 3, on figure 1.

Other than these correlations, there is only a very crude relationship among the dielectric data themselves: low overall loss generally means high resistivity and high dielectric strength.

Besides the limited knowledge about correlations between structure and dielectric properties, we are often not free to establish the dielectric properties we want, for instance, low polarity, because polar groups are often needed to obtain good physical properties.

It is felt, therefore, that in the early stages of the development of a material the dielectric properties play a secondary role and that emphasis should be directed towards thermal stability. This has already been pointed out by Dr. Evans at the Dallas Meeting in 1958 and is still valid. Fortunately, we know much more about promising structures for thermal stability than for good dielectric properties. Here, however, considerable difficulties are involved with the synthesis of the desired structures.

Figure 2 shows a number of structures which we would consider promising for thermally stable polymers. Novel inorganic structures include the Si-N, Al-O, and P-N backbone, while favorable organic structures contain aromatic, cycloaliphatic, and heterocyclic systems, or conjugated double bonds. A majority of these structures have been synthesized already; however, most of these are of rather low molecular weight, which means that the mechanical properties are also low. We have to find new procedures to raise the molecular weight of these structures to obtain materials for practical applications. The thermal stability of these novel polymers, however, is very promising. Figure 3 represents weight loss curves obtained in the thermobalance. In the thermobalance, a sample of the material is heated increasing the temperature at a constant rate, in this case 150° C/hour, under nitrogen. The weight loss of the material is an indication of its stability against degradation. The figure shows the weight loss curves of the two most stable conventional polymers, a polysiloxane, and polytetrafluoroethylene, compared with one of the most promising novel polymers, a polybenzimidazole (a pure organic structure).

We do not know anything about the dielectric constant, loss, and resistivity of these new polymers. The reason is that most of the structures have been developed only recently, or have not been obtained in optimal purity. Furthermore, we had no reliable method so far to obtain reliable and reproducible dielectric measurements from small amounts of powderous materials. Recently however, under Air Force contract, procedure and electrodes for the determination of dielectric constant, dielectric loss and resistivity in

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temperature and frequency dependence of experimental materials have been developed. Powders are compacted in special cells under pressures of 15,000 to 18,000 psi and the electrical measurements carried out by using painted silver, circular electrodes. Temperature ranges are between room temperature and approximately 400°F, the frequency range between 60 cycles and 1 megacycle.

The outcome of the testing of some of the experimental materials will be of considerable interest. There are indications to assume that some of the organic structures shown on figure 2 are semiconductors rather than insulators. According to the present theories, aromatic structures such as the benzene ring and conjugated systems of double bonds permit shifting of electrons from place to place and should therefore be conducting, provided that a path exists to move electrons from one ring or chain to the next. The fused ring structure of graphite is a good example for this principle. It is therefore possible, that structures of prevailing aromatic or conjugated structure, and perhaps also organometallic polymers, are potential semiconductors, and that we might find novel insulating materials preferably in the field of inorganic polymers. However, it is too early to make predictions.

What we need for the near future (and this is part of our present research program) is (a) to synthesize novel, thermally stable polymeric structures and (b) to collect data of dielectric properties of these experimental materials, to establish a better background on structure-property relationships.

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CORRELATION BETWEEN STRUCTURE and DIELECTRIC PROPERTIES , (1)

- High Dielectric Constant = High Dipole Concentration
  Low Dielectric Constant = Low Dipole Concentration
- Dielectric Relaxation (o) And Second Order Transition Point (x)

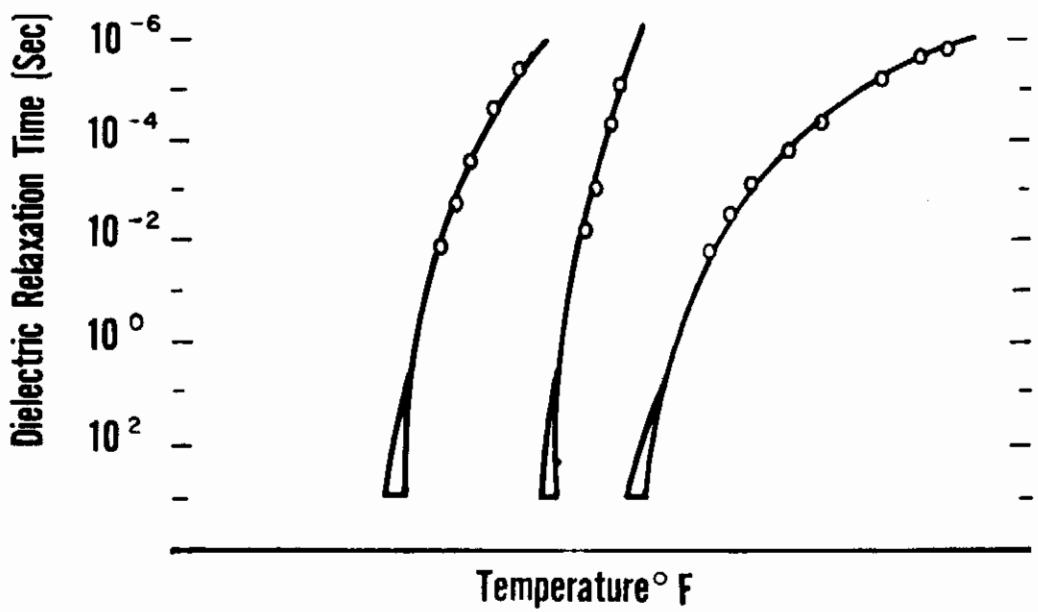

Figure 1.

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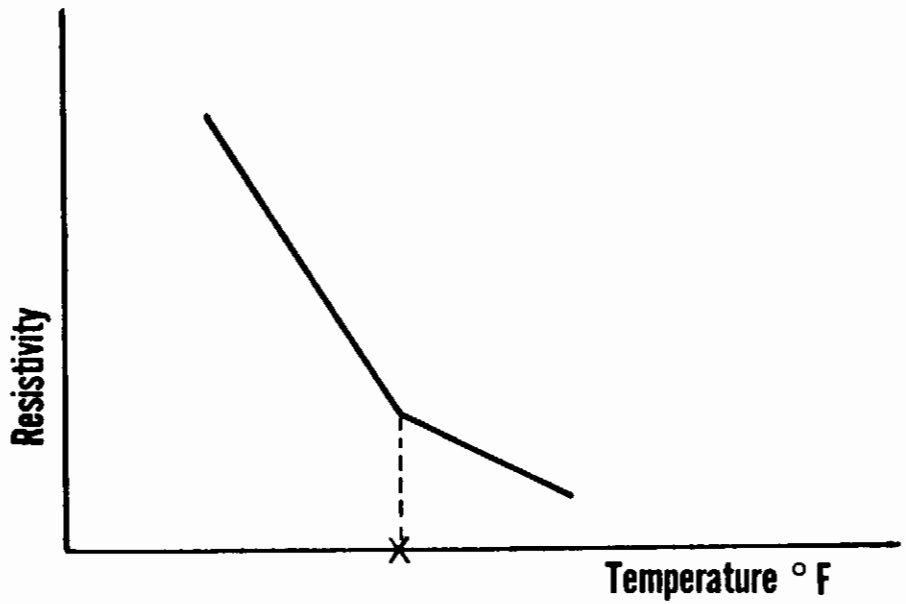
CORRELATION BETWEEN STRUCTURE and DIELECTRIC PROPERTIES, (2)

- Resistivity And Second Order Transition Point (×)



- Low Loss High Resistivity High Dielectric Strength
- High Loss Low Resisting Low Dielectric Strength

Figure 1. (Cont'd)

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EXAMPLES of THERMALLY STABLE POLYMERIC STRUCTURES

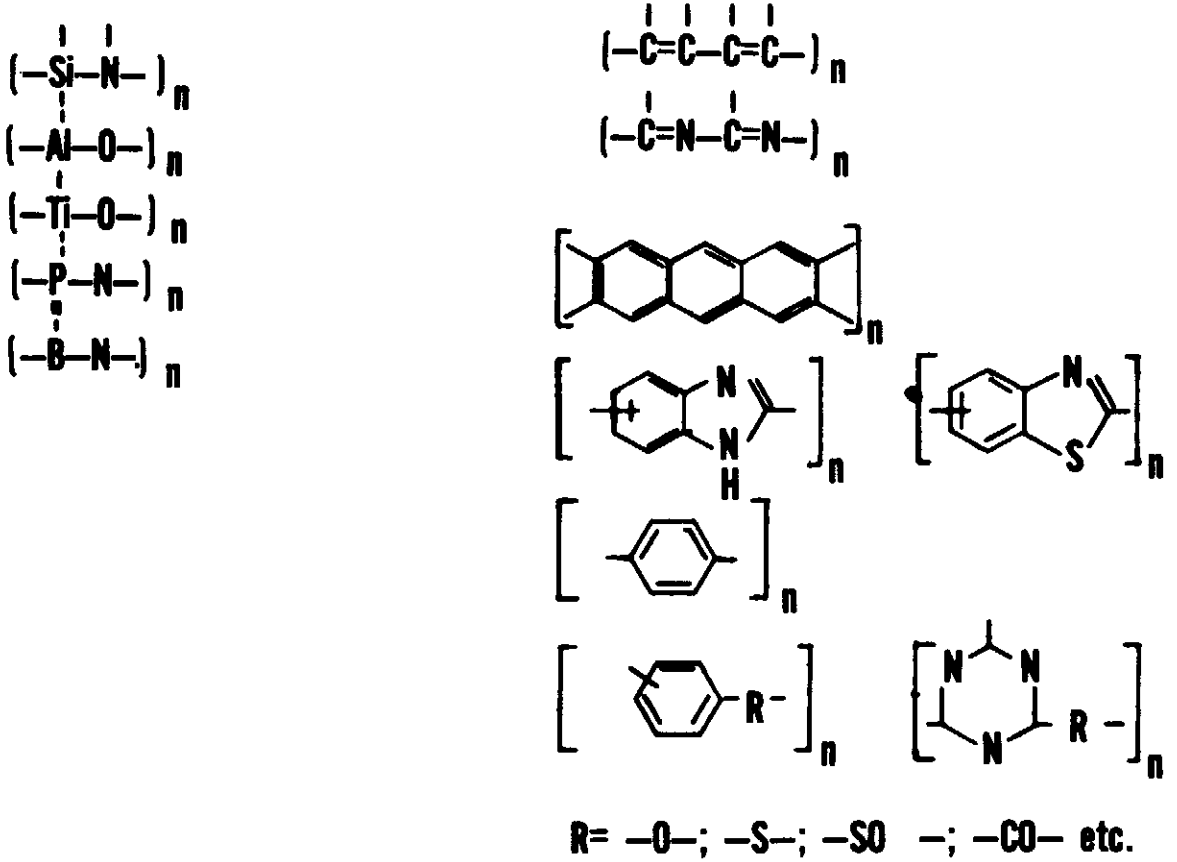

Figure 2.

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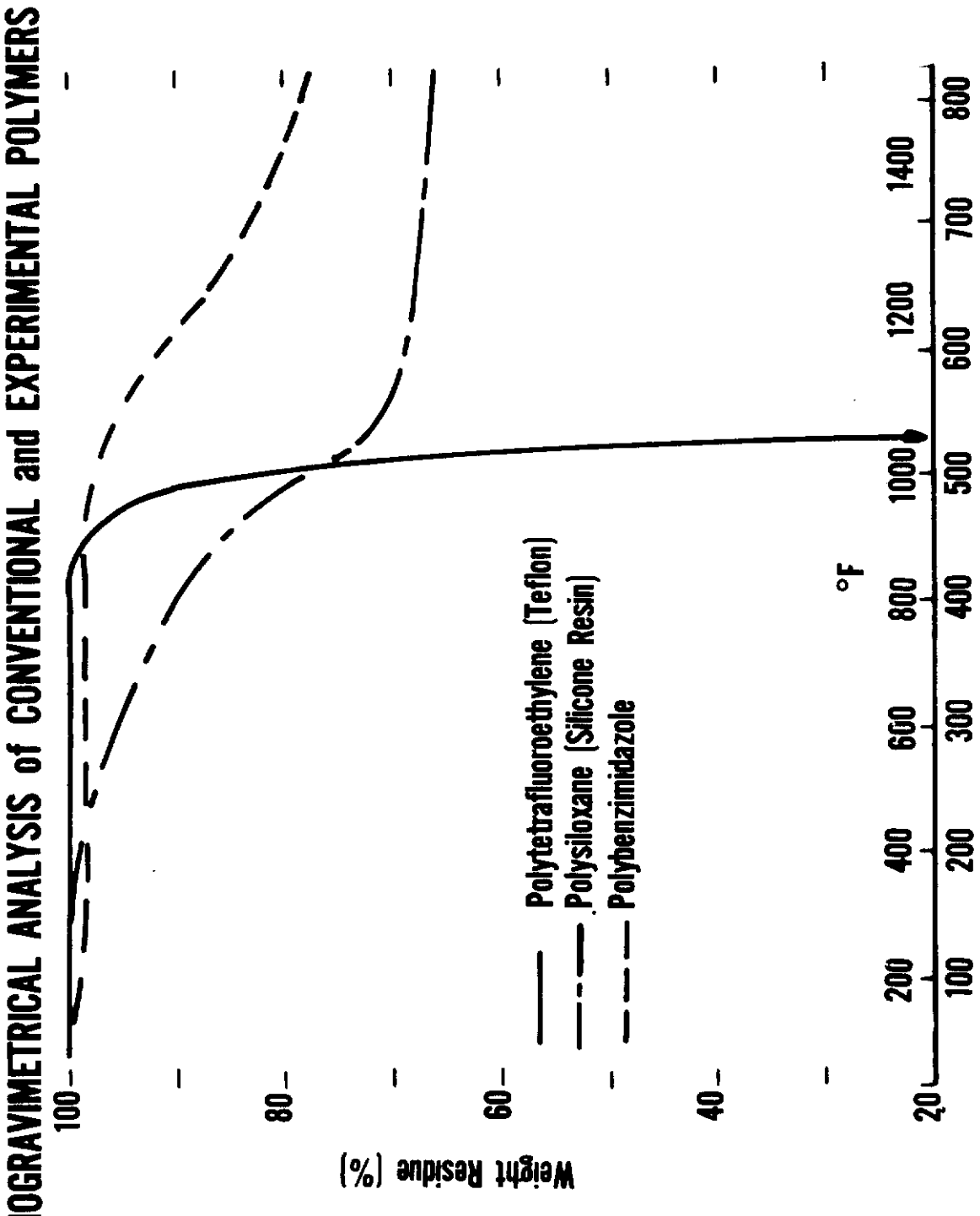

Figure 3.

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